

REACTIVE INTERMEDIATES IN COAL LIQUEFACTION

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INTRODUCTION: Investigations into the mechanisms of coal liquefaction are hampered by the difficulty in obtaining information at the molecular level. The chemical structure of the starting coal is poorly defined and the products can be only partially identified. Traditionally, mechanisms have been discussed in terms of the yields of phenomenologically defined fractions such as oils (pentane soluble product) and asphaltenes (pentane insoluble, benzene soluble products). While these pseudo-components have practical importance, their relation to molecular processes is unsure. An approach to understanding the physical organic chemistry of liquefaction using a method to monitor the presence of reactive intermediates has shown promise (1,2). This approach makes use of probe compounds to measure the prevalence of selected reactive intermediates. A further extension of this work is described here.

Compounds which can be shown to give distinct products upon reaction with different reactive intermediates are selected to probe for the presence of those intermediates. For example, 1,5-dimethylnaphthalene undergoes de-methylation in the presence of hydrogen atoms, hydrogenates to the methyltetralins in the presence of catalytic hydrogenation sites, and undergoes rearrangement of the methyl groups to give the 1,6- and 2,6-dimethyl isomers in the presence of acids or acidic catalyst sites (2). Equally important is the fact that little or no product cross-over occurs. That is, little isomerization is found in the presence of a good radical initiator and little or no de-methylation is found in the presence of an acid catalyst. Thus, the occurrence of isomerized methylnaphthalenes among the reaction products is indicative of the presence of cationic pathways, and the occurrence of methylnaphthalenes is indicative of the presence of hydrogen atoms and/or hydrogen atom donors.

The question of whether or not structures resembling dimethylnaphthalene are present in coal is immaterial. The purpose of the probe compounds is to detect the presence of reactive intermediates, not to mimic a bond thought to be present in the coal. This differentiates the probes from the model compounds often seen in the literature. Thus, while 1,6-dimethylnaphthalene may

bear some resemblance to a coal model compound, it is only one example of compounds which can be used as mechanistic probes. Other compounds previously used as probes include 1,3-dimethylnaphthalene(1), *cis*-decalin(1,2), and a tricyclodecane(2). The tricyclodecane is a good example of a probe with no coal-like bonds. The fact that little if any evidence exists for tricyclic compounds in coal has no effect on its ability to distinguish the presence of reactive free radicals.

EXPERIMENTAL: The compounds used as probes were obtained from Aldrich and contained less than 1% impurities as determined by GC. They were used without further purification. The commercial silica alumina (D980-13) was obtained from W.R. Grace (grade 980-13, 13% alumina) as an extrudate. The friable solid was ground with a mortar and pestle, and oven-dried at 150°C overnight. The molybdenum trisulfide was prepared from ammonium tetrathiomolybdate by precipitation from an aqueous solution using formic acid.(3) This procedure is best carried out in a hood because of the hydrogen sulfide formed. The ammonium tetrathiomolybdate obtained from Aldrich was used without further purification.

All reactions were performed using 40-mL 316-stainless steel reactors. The 8-gram reaction mixtures contained the probe (200 mg); a silica-alumina (10 mg), molybdenum trisulfide (10 mg), bibenzyl (2.0 g), or coal (up to 1.5 g Ill. No.6) additive; and n-octacosane solvent. The reactors were pressurized to 1200 psig with hydrogen, heated to 425°C within 5-6 minutes by plunging them into a preheated fluidized sand bath, and shaken at temperature for 60 minutes. The products were washed from the cooled reactor using inhibitor-free tetrahydrofuran (Aldrich 27,038-5). The reaction mixtures were analyzed by GC-MSD using a Hewlett-Packard 5890 GC with a model 5970B MSD operated in the total ion mode. The GC quantitation was performed using internal standards with an estimated error of $\pm 3\%$. The analysis of the coal has been reported.(1)

RESULTS AND DISCUSSION: One of our first probe studies of liquefaction mechanisms used 1,3-dimethylnaphthalene to demonstrate that the selectivity of the hydrogen atom mediated hydrocracking reaction is increased in the presence of coal.(1) This probe produces 1-methylnaphthalene upon hydrogen atom attack at the 3-position and 2-methylnaphthalene upon attack at the 1-position. The effect of added coal is shown in Figure 1 where the percent yields of the mono-methylnaphthalenes are plotted as a function of the amount of added Illinois No.6 coal. Separate experiments without added probe showed that less than 15% of the increase was due to coal derived material co-eluting with the methylnaphthalenes. The increase in the total yield of methylnaphthalenes (top line) with added coal indicates that the net effect of the added coal is to enhance the amount of hydrogen atom transfer to the probe. The ability of the coal to produce hydrogen atoms or

hydrogen atom donors is greater than its ability to consume them. This additional activity results in the production of mostly 2-methylnaphthalene. As can be seen from the plots of the individual isomers (lower lines), the production of 1-methylnaphthalene remained relatively constant. Thus, the addition of the coal affects not only the prevalence of the hydrogen atom reactions but also the selectivity with which they occur. This change in selectivity has been associated with the nature of the hydrogen atom donor. (1)

More recently, our efforts have been devoted to exploring the changes in mechanism associated with the addition of liquefaction catalysts. (2) These systems are expected to be even more challenging than the thermal systems because cationic processes may become important in the presence of added catalysts. Cationic processes generally are not considered to be important in the thermal reactions of coal. Indeed, our previous work showed no evidence of cationic activity strong enough to result in the rearrangement of the 1,3-dimethylnaphthalene. (1) Added liquefaction catalysts may contain acid sites associated with the catalyst supports or with the metal sulfides themselves. Mild cationic character has been associated with an unsupported molybdenum sulfide hydrogenation catalyst. (4) Mechanistic probes should provide evidence to substantiate or refute the importance of cationic processes during catalytic liquefaction.

A probe chosen to distinguish among several mechanisms was 1-ethylnaphthalene. Products that may be obtained from this probe by various pathways are shown in Figure 2. That the products can be related to the presence of distinguishable reactive intermediates was established by the data given in Table I. In the absence of any additive, a small amount of hydrogenation to the ethyltetralins (4%) and de-alkylation to naphthalene (6%) occur but the majority of the recovered material is un-reacted 1-ethylnaphthalene. The effect of the addition of the known radical initiator, bibenzyl, is to increase the naphthalene yield. Since the reaction is carried out under hydrogen, the increased de-alkylation is attributed to the hydrogen atom mechanism proposed by Vernon. (5) However, the addition of the free radical source affected neither the yield of rearranged nor the yield of hydrogenated products. In contrast, the addition of the commercial silica alumina catalyst, D980-13, caused a dramatic increase in the extent of rearrangement. While the amount of ethylnaphthalene recovered is the same as in the blank, 62%, the major portion of it has been isomerized to the 2-isomer. Significantly, no increase in the extent of de-alkylation nor in the extent of hydrogenation was observed. Thus, the isomerization to form the 2-ethylnaphthalene can be used as an indication of the cationic activity since this product is formed in the presence of the silica alumina catalyst but not in the presence of the radical initiator. Similarly, the formation of naphthalene can be used as an indication of the extent of hydrogen atom activity since it is formed in the presence of the bibenzyl initiator but not in the presence of the silica alumina catalyst.

The above comparisons serve as the basis for the interpretation of the results obtained in the presence of other catalysts. Our initial investigations have focused on molybdenum trisulfide. This material is used as a precursor to the molybdenum disulfide which is formed under the reaction conditions.(6) The disulfide is thought to be the active form of the catalyst. Molybdenum trisulfide has been shown to be an effective liquefaction catalyst precursor under typical reaction conditions.(7) The fourth column of data in Table I shows the results obtained for this molybdenum sulfide catalyst. The appearance of rearranged ethylnaphthalene among the reaction products indicates that the molybdenum sulfide has some cationic character. Although the absolute amount of 2-ethylnaphthalene is only 6%, it accounts for over 25% of the additional products formed in the presence of the sulfide and is well above that formed in the absence of any additive or in the presence of bibenzyl. The yield of naphthalene is the same as was found in the blank; the molybdenum sulfide does not appear to enhance nor diminish this hydrogen atom mediated reaction. The main effect of the molybdenum trisulfide is to enhance the extent of hydrogenation as evidenced by the increased yield of ethyltetralins. The hydrogenation activity displayed by the trisulfide may involve acid sites or proton transfer to the substrate, but the hydrogenation probably does not proceed via a hydrogen atom transfer to produce a free hydronaphthyl radical.

Whether there is an intimate link between the observed hydrogenation and cationic activities or whether they are simply parallel, unrelated reactions cannot be determined from the above data. It has been proposed that anion vacancies are necessary for the binding of the substrate prior to hydrogenation.(8) Also, the chemisorbed hydrogen on the catalyst surface has been described as acidic hydrogen.(9,10) To further investigate the correlation of cationic behavior with hydrogenation behavior, the effect of added quinoline on the extent of these reactions was determined. These data are shown in Figure 3 where the yields of these two classes of products are plotted against the amount of added quinoline expressed as its molar ratio to molybdenum. The two graphs are remarkably similar. Added quinoline has little effect up to a ratio of about 1. Higher levels of addition cause decreased yields of both rearranged product and hydrogenation products. Thus, it appears that the acidic character of the molybdenum sulfide and its hydrogenation ability are correlated. Whether this correlation is causative cannot be determined from these data, but the results are very suggestive. The amount of quinoline needed to affect the catalyst activity was high. It was anticipated that inhibition of activity would occur at much lower levels of base because the active sites are on the catalyst surface only. Since stoichiometric amounts of base were needed to inhibit the hydrogenation activity, a simple interpretation based on non-competitive poisoning of the surface sites is insufficient to explain the observed inhibition.

CONCLUSIONS: The use of probe compounds in the study of coal liquefaction provides mechanistic details unavailable through the more traditional approaches. The approach has been applied to the study of the thermal liquefaction of coal and to liquefaction catalysts in the absence of coal. The current application to molybdenum sulfide catalysis has shown the precursor, molybdenum trisulfide, to be inactive in promoting free radical reactions. The dominate hydrogenation activity of the catalyst appears to be closely associated with its mild acidic character. Studies extending the technique to other catalysts and to catalytic coal liquefaction are currently under way.

DISCLAIMER: Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the U.S. Department of Energy.

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TABLE I. Product Distribution from 1-Ethyl-naphthalene (mole %).

	Additive			
	None	Bibenzyl	D980-13	MoS ₃
1-Ethyl-naphthalene	62%	69%	19%	64%
2-Ethyl-naphthalene	1	1	43	6
Naphthalene	6	19	3	7
Ethyl-tetralins	4	3	1	17
1- & 2-Methyl-naph.	<u>1</u>	<u>4</u>	<u>1</u>	<u>1</u>
RECOVERY	73%	96%	67%	95%

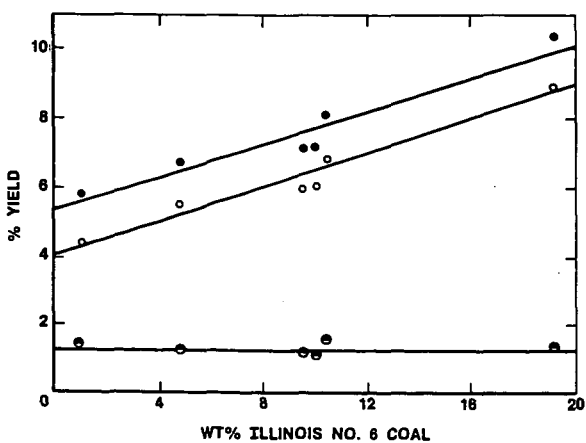


FIGURE 1.

NO. 19-371

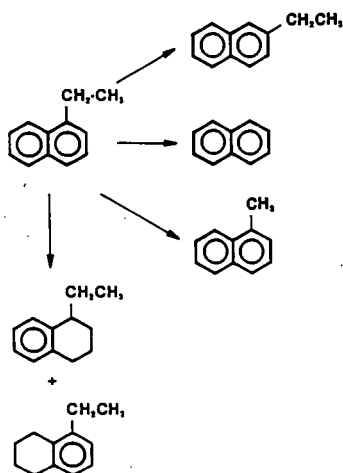


FIGURE 2.

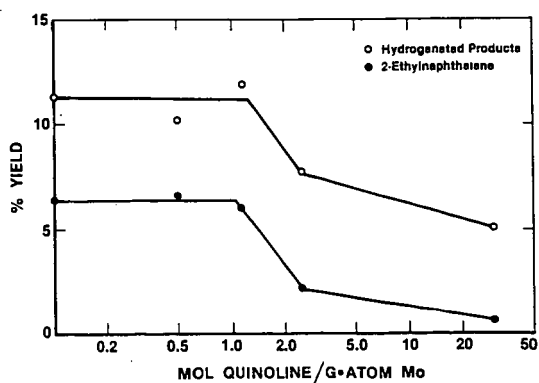


FIGURE 3.